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CORRELATED AND SQUEEZED VIBRATIONAL STATES IN POLYATOMIC MOLECULES [1,2]

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It is shown that different types of nonclassical vibrational states including quadrature and amplitude squeezed, entangled and Schrödinger cat states emerge during laser pulse excited Franck-Condon transitions in molecules.

1. Introduction

Recent progress in ultrafast optics [1,2] opened new possibilities in the control and observation of real-time molecular dynamics. There are both theoretical [3-7] and experimental [8-13] investigations of these problems. In recent papers it was shown for diatomic molecules that depending on the change of the geometrical configuration of the potential curves and the characteristics of the light pulse, a Franck-Condon transition may result in vibrational quadrature or amplitude squeezed states with different properties [14]. The possibility of preparing other nonclassical vibrational states in diatomic molecules has also been investigated.

In this paper we review the preparation of nonclassical vibrational states in molecules. A displacement of the equilibrium nuclear distances due to the excitation of the electronic system leads to vibrations of the nuclei. The change of the vibrational frequencies also results in vibrations even if there is no displacement of the equilibrium positions. We determine the time-evolution operator and the emerging vibrational state of a polyatomic molecule in a Franck-Condon transition when the electronic system is excited with a transform limited, weak light pulse. The potential surfaces are approximated with general harmonic potentials. We show that depending on the duration of the excitation pulse and the parameters of the transformation of the nuclear potential the vibrational state will be vibrational Schrödinger-cat state, amplitude squeezed state,

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quadrature squeezed state, and vibrational entangled state. The von Neumann entropy of the states is introduced as a measure of the entanglement. An essential consequence of the entanglement is that there exist observables of the different vibrational modes that exhibit correlations.

2. Model Hamiltonian

The vibrational Hamiltonian of a polyatomic molecule consists of $3N-6$ harmonic oscillator Hamiltonians if the molecule is nonlinear and $3N-5$ if the molecule is linear, where N is the number of the nuclei in the molecule. Let us consider an N-dimensional system described by the Hamiltonian

$$\hat{H}_i = \frac{1}{2}\sum_{n=1}^{N}(\hat{p}_n^2 + \omega_n^2\hat{q}_n^2), \tag{1}$$

where $\hat{p}_n$ and $\hat{q}_n$ are the momentum and normal coordinate associated with the nth vibrational mode, and ω_n is the frequency of the vibration. First we summarize briefly how the vibrational state of the molecule can be found after a sudden change of the parameters describing the nuclear potential. We follow the derivation described in [15]. In general both the equilibrium distances and the harmonic force constants are altered. The new Hamiltonian has the following form

$$\hat{H}_f = \frac{1}{2}\sum_{n=1}^{N}\hat{p}_n^2 + \frac{1}{2}\sum_{n=1}^{N}\sum_{m=1}^{N}u_{nm}\hat{q}_n\hat{q}_m + \sum_{n=1}^{N}f_n\hat{q}_n. \tag{2}$$

Here $\hat{p}_n$ and $\hat{q}_n$ are the same dynamical variables as in Eq. (1).

A new coordinate system can be introduced by means of the linear transformation

$$\hat{\mathbf{q}}' = S\hat{\mathbf{q}} + \mathbf{d}, \tag{3}$$

in which the Hamiltonian Eq. (2) is diagonal. Here S describes a pure rotation and $\mathbf{d}$ is associated with the displacement of the normal coordinate system. The variables associated with the new coordinate system are denoted by an apostrophe.

The connection between the vectors $\mathbf{d}$ and $\mathbf{f}$ can be expressed as $\mathbf{d} = \Lambda^{-1}S\mathbf{f}$, where the matrix $\Lambda = \mathrm{diag}\{\omega_n'^2\}$ contains the vibrational frequencies of the molecule in the new normal coordinate system. In the end the final Hamiltonian reads

$$\hat{H}_f = \frac{1}{2}\sum_{n=1}^{N}(\hat{p}_n'^2 + \omega_n'^2\hat{q}_n'^2) - H_0, \tag{4}$$

where $H_0 = \mathbf{d}\Lambda\mathbf{d}$. H_0 arises from the translation of the equilibrium distances.

There is a unitary transformation denoted by $\hat{\Sigma}$ which connects both the initial and final Hamiltonian of the system and the state vector in the initial and in the final coordinate system [15]:

$$\hat{H}_f = \hat{\Sigma}^\dagger\hat{H}_i\hat{\Sigma}, \quad |\Psi\rangle_f = \hat{\Sigma}^\dagger|\Psi\rangle_i. \tag{5}$$

This unitary transformation in the Hilbert space is equivalent to the linear transformation of the normal coordinates in Eq. (3).

Let us consider the problem of the Franck-Condon transition in a polyatomic molecule excited with a transform limited light pulse described by the electric field

$$E(t) = E_0\exp(-u^2t^2/2)\cos(\Omega t), \tag{6}$$

where E_0 is the maximal amplitude and Ω is the mean frequency of the pulse. The duration of the pulse is proportional to u^{-1}. In the rotating wave approximation the vibrational Hamiltonian for the excited electronic level including the resonant interaction with the external classical field is

$$\hat{H}_f' = \hat{H}_f + \hat{V}(t), \tag{7}$$

where $\hat{H}_f$ is the Hamiltonian in Eq. (4), and the interaction potential $\hat{V}(t)$ is defined by

$$\hat{V}(t) = \frac{1}{2}E_0\exp(-u^2t^2/2)[e^{-i\Omega t}d_{ge}\,|\,g\rangle\langle e\,|\,+e^{i\Omega t}d_{eg}\,|\,e\rangle\langle g\,|]. \tag{8}$$

Here $|\,g\rangle\langle e\,|$ and $|\,e\rangle\langle g\,|$ are electronic state creation and destruction operators, d_{ge} is the electronic dipole matrix element.

Suppose that the molecule initially is in the ground electronic and vibrational state $|\,0\rangle_i\,|\,g\rangle$. An exciting pulse whose duration is much shorter than the period of the vibrations arrives at $t=0$. Then the time-evolution operator $\hat{U}(t)$ associated with the vibrations of the nuclei in the excited electronic level can be obtained in the form

$$\hat{U}(t) = e^{-i\hat{H}_ft}\hat{\Sigma}^\dagger. \tag{9}$$

$\hat{\Sigma}^\dagger$ transforms the ground vibrational state from the initial coordinate system to the final one then the operator $\exp(-i\hat{H}_ft)$ evolves the state in the upper level. Though the vibrational coordinates are independent of each other the vibrations in the constituent modes start to evolve at the same time.

For a finite exciting pulse assuming weak electric field, one can calculate the time-evolution operator of the vibrational system using the first order time-dependent perturbation theory. It is found that this operator is the convolution of the weak interaction potential $\hat{V}(t)$ in Eq. (8) and the time-evolution operator $\hat{U}(t)$ in Eq. (9):

$$\hat{T}(t) = \frac{1}{2}E_0d_{eg}\int_{-\infty}^{t}d\tau\,\exp(-u^2\tau^2/2)e^{i(\Omega-\omega_{eg})\tau}\hat{U}(t-\tau), \tag{10}$$

where $\hbar\omega_{eg}$ is the energy difference between the electronic levels. After the exciting pulse has passed, i.e., for the time $t \gg u^{-1}$ the integral can be evaluated. Finally, we obtain the operator $T(t)$ in the form

$$\hat{T}(t) = \mathcal{N}e^{-\frac{(\hat{H}_f-\gamma)^2}{2u^2}-i\hat{H}_ft}\hat{\Sigma}^\dagger, \tag{11}$$

where $\gamma = \Omega - \omega_{eg} - H_0$, and $\mathcal{N}$ is an unimportant integration constant. The non-unitarity of the operator results from the perturbative method. The emerging vibrational state in the upper level is

$$| \psi(t)\rangle_f = \hat{T}(t) \mid 0\rangle_i. \tag{12}$$

This state is unnormalized since $\hat{T}(t)$ is non-unitary. We note that Eq. (12) is valid for any polyatomic molecule since we did not exploit the dimensionality of the system during the derivation. The quantity ${}_f\langle\psi(t) \mid \psi(t)\rangle_f$ is the probability of finding the molecule in the excited state after the pulse has passed.

3. Diatomic molecules

Let us consider diatomic molecules i.e. when $N = 1$ in Eq. (1). In Eq. (2) the matrix $\{u_{nm}\}$ is replaced by a single frequency ω'^2. In this case the operator $\hat{\Sigma}$ describes the displacement of the equilibrium nuclear distance and the change of the vibrational frequency from ω in the ground electronic state to ω' in the excited electronic level.

Let us assume that the vibrational frequency does not change during the transition. The emerging vibrational state, depending on the pulse duration, corresponds to several of the most important states in quantum optics. In the case of extremely short pulses the wave function is a usual coherent state while in the opposite limit of long pulses it is the n-phonon number state. Between these limiting cases it is close to a quadrature squeezed minimal uncertainty state, or, for longer pulses it is the banana-like amplitude squeezed state, which also appears to be an approximate number-phase intelligent state associated with Pegg-Barnett phase operator formalism.

If the vibrational frequency changes during the transitions the half-width of the wave packet is different from that of the coherent state of the upper level:

$$\Delta\hat{q}' = \sqrt{\frac{\hbar}{2\omega}} \neq \sqrt{\frac{\hbar}{2\omega'}} = \Delta\hat{q}'_{\rm coh} \tag{13}$$

The half-width of this wave packet spreads and contracts periodically in time with the period time half of the vibrational period. This state is a quadrature squeezed coherent state. When $d = 0$ we have a quadrature squeezed vacuum state.

Let us now consider two identical Gaussian shaped pulses following each other by an interval T_1

$$\begin{aligned} E(t) &= E_0 e^{-\frac{u^2}{2}(t+\frac{T_1}{2})^2} \cos\left(\Omega(t+\tfrac{T_1}{2})\right) \\ &+ E_0 e^{-\frac{u^2}{2}(t-\frac{T_1}{2})^2} \cos\left(\Omega(t-\tfrac{T_1}{2}-\phi)\right), \end{aligned} \tag{14}$$

here ϕ is a possible additional phase difference between the subpulses.

The vibrational state produced by such a twin pulse excitation has the form

$$\begin{aligned} | \{u, T_1, \gamma, \phi\}\rangle &= e^{-i\omega_{eg}\frac{T_1}{2}} \mid u, (t+\tfrac{T_1}{2})\rangle + e^{i\omega_{eg}\frac{T_1}{2} - i\phi} \mid u, (t-\tfrac{T_1}{2})\rangle, \\ | u, t\rangle &= \int_{-\infty}^{\infty} d\tau\, e^{-\frac{u^2}{2}\tau^2 + i\gamma\tau)} \mid \alpha(\tau - t)\rangle_{coh}. \end{aligned} \tag{15}$$

It is assumed, that the vibrational frequency does not change during the transition.

For extremely short pulses we have coherent superposition states which are the vibrational analogue of the optical Schrödinger cats states. For long, strongly overlapping pulses Eq. (15) leads to the phonon number state.

By a secondary excitation using probe pulse(s) one may transfer the vibrational cat state into chemical cat state creating quantum superpositions of different molecules. In Ref. [10] an Na_2 molecule was excited by a short laser pulse. Applying a second laser pulse the state was excited once more. Depending on the time delay between the two successive pulses the resulting state was a molecule on another excited level or dissociated fragments. We suggest an experiment in which double pulse primary excitation leads to a Schrödinger-cat vibrational state in level e. Applying a third pulse when the two parts of the Schrödinger-cat state are the furthest from each other one obtains a superposition of the molecule with its fragments. This chemical cat state can lead us very near to the original paradox of Schrödinger. Let us suppose that this molecular superposition is superposition of the undamaged form of a virus's DNA with a denaturalized variant of the same virus. The resulting "Schrödinger virus state" would be, in fact, a quantum mechanical superposition of a "living" and a "dead" virus.

4. Polyatomic molecules

For the sake of simplicity we shall consider a two-dimensional system. This model describes nonlinear XY_2 molecules performing totally symmetric vibrations. The vibrational state in Eq. (12) for a two-dimensional system can be found by inserting a complete basis set between the exponent part and $\hat{\Sigma}^\dagger$ in the time-evolution operator $\hat{T}(t)$ of Eq. (11):

$$\begin{aligned} | \psi(t)_f\rangle &= \mathcal{N} \textstyle\sum_{n_1', n_2'} e^{-\frac{(\hat{H}_f - \gamma)^2}{2u^2} - i\hat{H}_f t} \mid n_1', n_2'\rangle_{ff}\langle n_1', n_2' \mid \hat{\Sigma}^\dagger \mid 00\rangle_i \\ &= \mathcal{N} \textstyle\sum_{n_1', n_2'} F'_{n_1' n_2'} e^{-\frac{(n_1'\omega_1' + n_2'\omega_2' - \gamma)^2}{2u^2} - i(n_1'\omega_1' + n_2'\omega_2')t} \mid n_1', n_2'\rangle_f. \end{aligned} \tag{16}$$

Here the matrix elements

$$F'_{n_1' n_2'} = {}_f\langle n_1', n_2' \mid \hat{\Sigma}^\dagger \mid 00\rangle_i, \tag{17}$$

can be determined by the recurrence formulas in Ref. [15].

The final vibrational state Eq. (16) depends on the duration of the exciting pulse u^{-1} and the parameters of the transformation of the nuclear potential, that appear in the matrix elements $F'_{n_1' n_2'}$ in Eq. (17). When the duration of the pulse is very short the time evolution operator $\hat{T}(t)$ in Eq. (11) reduces to $\hat{U}(t)$ in Eq. (9). In this case the properties of the state vector Eq. (16) are more apparent in the coordinate representation. Using Eq. (3) and the wave function of the ground vibrational state we find that the vibrational wave function in the excited electronic level is

$$\Psi(q_1', q_2') = {}_f\langle q_1', q_2' \mid \hat{\Sigma}^\dagger \mid 00\rangle_i = \left(\tfrac{\omega_1\omega_2}{\pi^2\hbar^2}\right)^{\frac{1}{4}} e^{-\frac{1}{2}\mathbf{q}'L\mathbf{q}' + \mathbf{d}L\mathbf{q}' - \frac{1}{2}\mathbf{d}L\mathbf{d}}, \tag{18}$$

where $L = \frac{1}{\hbar}\begin{pmatrix} \omega_1\cos^2\chi + \omega_2\sin^2\chi & \frac{1}{2}(\omega_2 - \omega_1)\sin 2\chi \\ \frac{1}{2}(\omega_2 - \omega_1)\sin 2\chi & \omega_2\cos^2\chi + \omega_1\sin^2\chi \end{pmatrix}$.

A finite exciting pulse results in an entangled state because in Eq. (16) the exponential term can not be factorized when u is finite. A very short excitation can result in an entangled or non-entangled vibrational state depending on the configuration of the system.

Let us first determine the conditions when the vibrational state is not entangled. As we mentioned before, the shortness of the exciting pulse is a primary requirement. The wave function in Eq. (18) can only be separated to the product of two independent wave functions of the two constituent vibrational modes if the matrix L is diagonal. This case arises when either $\chi = 0$ or $\omega_1 = \omega_2$, i.e., either the normal coordinate system does not turn during the transition or the ground state vibrational potential has spherical symmetry.

As an example for a non entangled state induced by a very short pulse, let us consider the transition when there is only translation and no rotation and no dilatation of the normal coordinates ($\mathbf{d} \neq \mathbf{0}$, $\chi = 0$, $\omega_i = \omega_i'$). In this case the operator $\hat{\Sigma} = \hat{S}_t$ and the matrix L is diagonal. From Eq. (18) we find that the wave function is separable and the emerging vibrational state is a two-dimensional coherent state. The resulting state is also a two-mode coherent state if $\omega_1 = \omega_2$, $\chi \neq 0$, and the vibrational frequencies do not change. When there is not translation ($\mathbf{d} = \mathbf{0}$) in these transitions, the resulting state is the vibrational vacuum state.

If the vibrational frequencies change in the previous transitions the emerging vibrational wave function is also the product of two Gaussian wave packets. But the half-width of these wave packets are different from that of the coherent state of the upper level in the ith mode (Eq. (13)). When $\mathbf{d} = \mathbf{0}$ we have two independent quadrature squeezed vacuum states in each vibrational modes.

There exist geometrical configurations when a short exciting pulse leads to an entangled state. This is the case when $\omega_1 \neq \omega_2$ and $\chi \neq 0$ in Eq. (18) and $\mathbf{d}$ is arbitrary, that is, the normal coordinate system turns during the transition and the ground state potential is non-spherical. Then the off-diagonal elements of the matrix L do not vanish and the resulting vibrational wave function is given in Eq. (18).

If a system is in an entangled state, the partial systems are in mixture states though the whole system can be in a pure state. One can use the von Neumann entropy as a measure of the purity of the state of a vibrational mode:

$$S(\hat{\rho}_i) = -\mathrm{Tr}(\hat{\rho}_i \ln \hat{\rho}_i), \tag{19}$$

where $\hat{\rho}_i$ is the density matrix of the ith mode. $S(\rho_i) = 0$ for a pure state. In our case the origin of the non-purity is the entanglement of the vibrational modes. The sum of the two entropies provides a good measure for the degree of the entanglement

$$0 \leq S(\hat{\rho}_1) + S(\hat{\rho}_2). \tag{20}$$

Deeper entanglement results in larger entropies. The density matrix of the whole system is $\hat{\rho} = \mid \Psi\rangle\langle\Psi \mid$. It can be proved that the von Neumann entropies $S(\hat{\rho}_i)$ of the two partial systems are equal to each other for every possible transitions.

In our previous example the rotation of the non-spherical potential leads to an entangled vibrational state. It should be noted that the larger is the angle of rotation the more entangled the state is.

Now we turn to the problem of finite exciting pulse. In this case the vibrational state in Eq. (16) can not be separated to the product of two vibrational states, so the state is entangled independently of the change of the geometrical configuration. In geometrical configurations where a short exciting pulse leads to a non entangled state, a finite pulse results in an entangled state. As an example, let us consider the two-mode vibrational coherent state, which is induced by a very short exciting light pulse

$$\mid \psi(t)_f\rangle = e^{-g_1^2/2 - g_2^2/2} \sum_{n_1', n_2'} \frac{g_1^{n_1'} g_2^{n_2'}}{\sqrt{n_1'! n_2'!}} \mid n_1' n_2'\rangle, \tag{21}$$

where $g_i = (\omega_i'/2\hbar)^{\frac{1}{2}} d_i$. Now let the duration of the pulse be finite. In this case the role of the quadratic part in the exponent in Eq. (16) becomes important. The von Neumann entropy analysis shows that a longer pulse leads to deeper entanglement.

If the duration of the exciting pulse is large compared with the vibrational periods then only those terms will survive the Gaussian cutoff in the expansion Eq. (21) for which $\gamma = \omega_1' n_1' + \omega_2' n_2'$. This is the so called CW limit, well known in the literature. The emerging vibrational states are determined by the solution of this equation for given vibrational frequencies and photon energy in the exciting light ($\gamma = \omega - \omega_{eg} - H_0$). If the ratio of the vibrational frequencies are not that of small integer numbers there is only one solution. In this case there is no entanglement, the modes are separable the vibrational state of the molecule is the product of two eigenstates. In case of small integers' ratio of the vibrational frequencies multiple solutions exists for appropriate values of γ. Now the arising vibrational state is entangled. In a degenerate case the two vibrational frequencies are the same. For the coherent state of Eq. (21) the act of the quadratic operator yields

$$\mid \Psi\rangle = \mathcal{N} \sum_{n_1' + n_2' = \gamma/\omega'} \frac{g_1^{n_1'} g_2^{n_2'}}{\sqrt{n_1'! n_2'!}} \mid n_1' n_2'\rangle. \tag{22}$$

We have described two types of processes which lead to an entangled vibrational state in a polyatomic molecule: in the first case the change of the geometrical configuration during a sudden electronic transition leads to entanglement while in the second case entanglement comes from the finite excitation process. There is a difference between these states that appears in the joint phonon number distribution. The joint phonon number distributions for a state induced by a short exciting pulse can be obtained from the matrix elements of the operator $\hat{\Sigma}^\dagger$:

$$P(n_1', n_2') = \mid \langle n_1', n_2' \mid \hat{\Sigma}^\dagger \mid 00\rangle \mid^2 \tag{23}$$

In the case of an entangled state induced by a short exciting pulse, the joint phonon number distribution can be calculated with the help of the recurrence formulae in Ref. [15]. For the finite exciting pulse the joint phonon number distribution associated with the state Eq. (22) is a binomial one

$$P(n_1', n_2') = \begin{pmatrix} n_1' + n_2' \\ n_1' \end{pmatrix} p_1^{n_1'} p_2^{n_2'}, \quad p_1 = \frac{g_1^2}{g_1^2 + g_2^2}, \quad p_2 = \frac{g_2^2}{g_1^2 + g_2^2}. \tag{24}$$

The difference between entanglement resulting from the change of the geometry and the finite excitation process is that while in the first case the joint photon number distribution function is spread along a $n_1' \sim n_2'$ line (correlation), in the second case the main axis of the photon number distribution is perpendicular to the $n_1' \sim n_2'$ line (anticorrelation).

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